

Magnetization anomalies in the superconducting state of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and the magnetic study of $\text{Sr}_2\text{GdRuO}_6$

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Abstract

d.c. magnetization measurements performed on a polycrystalline sample of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru-1212) showed distinct peaks of the magnetization upon entering the superconducting state. Since $\text{Sr}_2\text{GdRuO}_6$ (Sr-2116) is the precursor for the preparation of Ru-1212, a detailed investigation of the magnetic properties of Sr-2116 was carried out. Although similarities were observed in the magnetic behavior of Sr-2116 and Ru-1212 in the temperature range of the observed peaks, we can exclude, based on a quantitative comparison, that the anomalies observed for Ru-1212 are due to Sr-2116 impurities.

Key words: superconductivity, d.c. magnetization anomalies, $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, $\text{Sr}_2\text{GdRuO}_6$

PACS: 74.72.-h, 74.25.Ha, 75.50.-y

1 Introduction

The discovery of coexistence of superconductivity and weak ferromagnetism in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru-1212) [1–3] has triggered a large number of studies of the properties of this material. From all these studies it becomes obvious, that

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the preparation method plays a very important role, in particular as far as the superconducting properties of the compound are concerned. For example, there are reports of non-superconducting samples of Ru-1212 [4] as well as for samples, which exhibit bulk superconductivity [5]. A key compound for the preparation of Ru-1212 is $\text{Sr}_2\text{GdRuO}_6$ (Sr-2116), either as an intermediate product during the preparation of Ru-1212 [2,6], or used directly as a precursor [3]. The (nominal) valency of Ru in Sr-2116 (Ru^{5+}) minimizes the likelihood of formation of the itinerant ferromagnet SrRuO_3 during the preparation of Ru-1212 in the two-step process [2].

$\text{Sr}_2\text{GdRuO}_6$ belongs to the class of double perovskites of the general chemical formula $\text{A}_2\text{BB}'\text{O}_6$ (often called “2116” compounds because of their stoichiometry) with $\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$, $\text{B}=\text{Y}, \text{La}, \text{Nd}, \text{Eu}, \text{Gd-Lu}$ and $\text{B}'=\text{Ru}$. Their structure, as determined by neutron [7–11] and X-ray diffraction [12], is that of a distorted perovskite with monoclinic space group $\text{P}2_1/\text{n}$ and can be visualized as corner-sharing tilted oxygen octahedra alternately centered by B and B', while the bigger A ions are located in the area between the oxygen octahedra.

These compounds offer the rare opportunity to study the magnetic behavior of a 4d^3 electron system. Indeed, magnetic ordering of highly oxidized cations from the second transition series is quite unusual but Battle *et al.* [7–11] have shown, that the Ru^{5+} ions in these compounds order antiferromagnetically at low temperatures.

A particular interest for a more detailed investigation of the magnetic properties of $\text{Sr}_2\text{GdRuO}_6$ arises from the fact mentioned above, that this compound is involved in the preparation methods of the magnetic superconductor Ru-1212. In this work we investigate samples of Ru-1212 prepared using Sr-2116 as a precursor material and examine the origin of distinct peaklike anomalies in the d.c. magnetization curves of Ru-1212 upon entering the superconducting state. We conclude, that these peaks cannot be explained in terms of some of our precursor material remaining as an impurity phase in the superconducting samples. A tentative explanation of the origin of the peaks, based on the interpretation of our data on Sr-2116, is given.

2 Experimental

Polycrystalline samples of Ru-1212 were prepared following a two-step procedure. First, Sr-2116 was prepared from stoichiometric quantities of RuO_2 , Gd_2O_3 and SrCO_3 . The powders were mixed, calcined at 950°C in air, pressed into pellets and fired for 16 h at 1250°C in air. In a second step, the obtained Sr-2116 was mixed with CuO , pressed into pellets and fired for 120 h at 1060°C in flowing oxygen.

Resistance measurements were performed by a standard four-probe a.c. technique (at 22.2 Hz) on bar-shaped pieces cut from the pellets using silver paint contacts. a.c. susceptibility measurements were done with a home-made susceptometer using a standard lock-in technique at different field amplitudes.

d.c. magnetization measurements were done with a commercial SQUID magnetometer (Cryogenic Consultants Ltd. S-600), which allows measurements in the temperature range $1.6 \text{ K} \leq T \leq 300 \text{ K}$ in magnetic fields up to 6 T. For the low field measurements, a paramagnetic AuCr sample was used as a standard for the determination of the remanent fields in the magnet. An external current source (Knick DC-Current-Calibrator J152) was used to cancel the remanent and earth fields and apply the appropriate current, so that the desired field could be achieved.

The Ru-1212 piece studied in the magnetometer was powdered afterwards and the x-ray powder diffraction pattern was taken on a Philips X-pert diffractometer with primary beam Ge(111) Johanson monochromator using $\text{Cu K}\alpha_1$ radiation. Flat plate geometry was used with the sample sieved on vacuum grease on a low background quartz sample holder. The result shown in figure 1a indicates, that within the resolution of the instrument the sample is single phase with the impurity phases (if any) representing less than 3 % of the sample. The tetragonal lattice parameters (spacegroup P4/mmm) are $a = 3.837(4) \text{ \AA}$, $c = 11.56(1) \text{ \AA}$.

A similar X-ray scan was done for the Sr-2116 sample studied in the magnetometer with a Seifert XRD 3000 P diffractometer and revealed, that traces of the original Gd_2O_3 powder were still present in the sample. The room temperature lattice parameters for our Sr-2116 sample were (spacegroup $\text{P2}_1/\text{n}$) $a = 5.808(5) \text{ \AA}$, $b = 5.819(5) \text{ \AA}$, $c = 8.212(8) \text{ \AA}$, $\beta = 90.3(1)^\circ$.

X-ray powder diffraction data of a similarly prepared Sr-2116 sample at low temperatures were collected in transmission geometry at the high energy beamline ID15B of the European Synchrotron Radiation Facility (ESRF). X-rays of energy 90 keV were selected by a bent Si (511) monochromator, which focuses the beam in the horizontal plane [15]. The size of the beam was adjusted to several mm height and a width of 0.5 mm. A MAR 345 image plate reader was used as detector at a distance of approx. 730 mm from the sample. The wavelength was determined to 0.14668 \AA from a NBS-676 LaB_6 standard. The sample was contained in a 0.7 mm lithiumborate glass (glass No. 50) capillary and was rocked several degrees during the measurement in order to improve randomization of the crystallites. Data were taken at several temperatures down to 23 K. Data reduction was performed using the program FIT2D [16], resulting in diagrams of corrected intensities versus the scattering angle 2θ . It was observed, that the diffracted intensity was quite uniformly distributed over the Debye-Scherrer rings, ruling out severe grain size effects

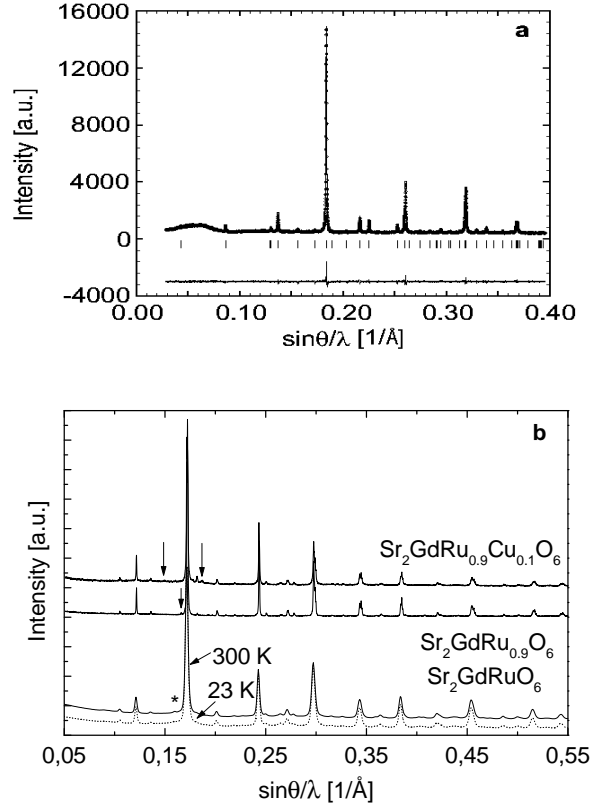


Fig. 1. **(a)** X-ray ($\text{CuK}\alpha$) diffraction spectrum of the Ru-1212 sample. The solid line is the LeBail fit [13] in space group $P4/mmm$ done using the program FULLPROF [14]. The peak positions and difference line are also shown. The amorphous hump at ~ 0.05 in $\sin\theta/\lambda$ is due to the vacuum grease. **(b)** X-ray patterns of Sr-2116 and related compounds. The asterisk indicates the position of the strongest peak of Gd_2O_3 and the arrows the positions of unidentified impurity peaks.

and preferred orientation. Low angle diffraction peaks had a FWHM of $0.04^\circ 2\theta$, which can be considered the highest resolution for this particular setup. At this high energy, no corrections for absorption are necessary. The data presented in the lower part of figure 1b show, that the crystal structure of the compound is stable at least down to 23 K.

3 Results and Discussion

3.1 Superconductivity and magnetism of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$

In figure 2 our resistivity and a.c. susceptibility results on Ru-1212 are shown. The resistivity measurements (inset) reveal a metallic behavior of the sample at high temperatures with a small cusp at about 135 K related to the magnetic transition, which occurs at this temperature (see d.c. magnetization

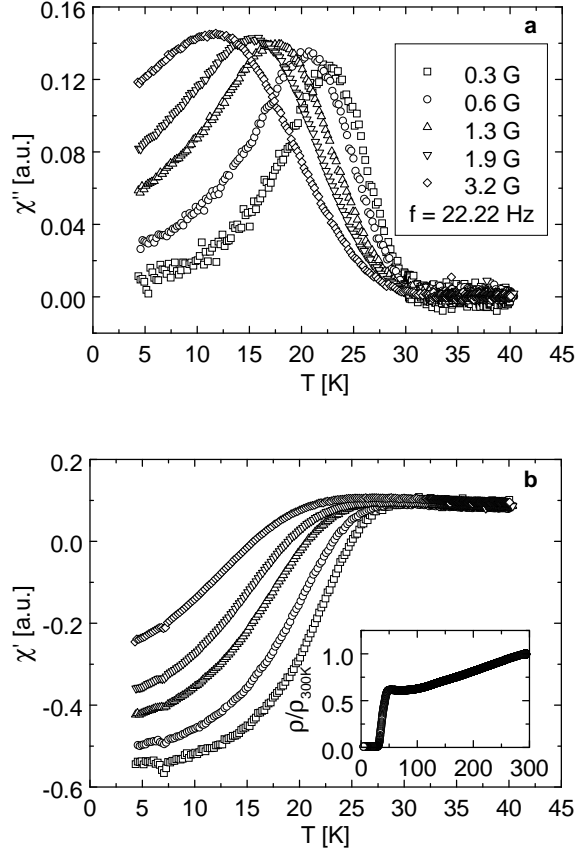


Fig. 2. The imaginary (a) and real (b) part of the a.c. susceptibility for Ru-1212 at low temperatures and different magnetic field amplitudes. Inset: resistivity data normalized to the room temperature value.

measurements presented below). At lower temperatures a slight upturn of the resistance is observed above the onset of superconductivity at 50 K, while the resistivity becomes zero at 30 K. At this temperature, the inter-granular coupling is established and a clear diamagnetic response is observed in the real part of the a.c. susceptibility with the corresponding loss peaks in the imaginary part. Typical for shielding due to inter-granular coupling, the transition widens and shifts to lower temperatures as the a.c. field amplitude is increased.

The results of d.c. magnetization measurements for three different measuring fields are shown in figure 3. At about 135 K, a magnetic transition is observed for the compound. The exact temperature of this transition depends on the applied field and decreases slightly from 137 K at 0.25 mT to 134 K at 10 mT. Although it was originally believed, that this transition is due to ferromagnetic ordering of the Ru moments, powder neutron diffraction studies [17–19] revealed an antiferromagnetically ordered state of the Ru moments and put a limit of about $0.1 \mu_B$ per Ru on any ferromagnetic component. The presence of a ferromagnetic component is indicated by hysteresis loops in M-H curves

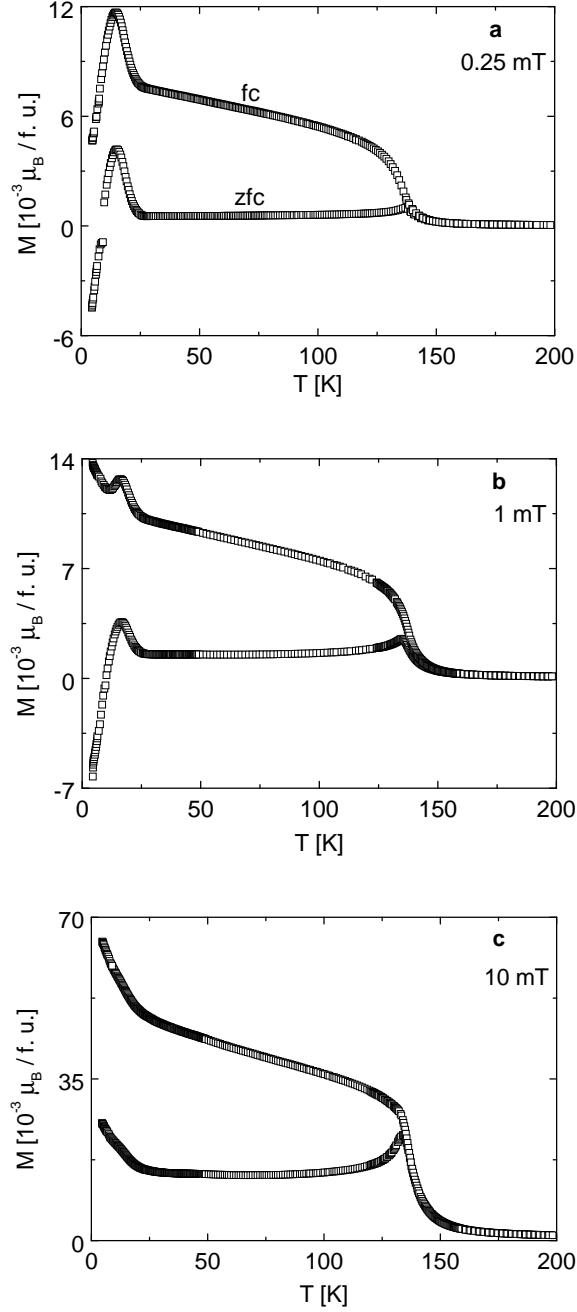


Fig. 3. Magnetic moment (in μ_B per formula unit) of our Ru-1212 sample at 0.25 mT (a), 1 mT (b) and 10 mT (c).

measured in the magnetically ordered state [6,19]. For these results to be consistent with the neutron diffraction data, the antiferromagnetically ordered Ru moments must be canted to give a net magnetic moment. This canting is thought to be associated with rotations of the RuO_6 -octahedra [3]. The zero field cooled (z.f.c.)-field cooled (f.c.) hysteresis observed for our M-T curves in the magnetically ordered state presumably arises [4] from an increased canting of the Ru moments due to the presence of the external magnetic field in the

f.c. process, which leads to higher values of the magnetization compared to the z.f.c. branch. The z.f.c.–f.c. hysteresis above about 30 K is also reminiscent of spin glass behavior and could involve freezing out of the canted component below the irreversibility temperature, which would be defined by the point, where the z.f.c. and f.c. curves merge.

In figure 3a, distinct anomalies of the magnetization are observed upon entering the superconducting state. The magnetization shows a clear increase at 25 K and reaches a peak at 15 K. In a low field (0.25 mT), the magnetization decreases below 15 K because of the field expulsion due to superconductivity. While the flux expulsion does not saturate down to our lowest measuring temperature, probably due to the small grain size ($\sim \mu\text{m}$) or possibly due to undetected sample inhomogeneity, it should be noted, that the signal corresponds to a complete flux expulsion from 25% of the sample volume. At 1 mT this peak is still observed but its height has decreased and at 10 mT no peak is present (although the curves show a cusp at low temperatures) and the flux expulsion characteristic of a superconductor entering the Meissner state has disappeared. Similar anomalies have also been observed by Klamut *et al.* [20]. Their sample had a slightly higher superconducting transition temperature of 35 K and the peak of the magnetization was observed at a higher temperature, above 25 K. In [20] two proposals were made, without further analysis, for the interpretation of the observed anomaly in the d.c. magnetization curve: (a) in terms of a change of the magnetic ordering of the Ru moments upon entering the superconducting state and (b) in terms of an anomalous flux lattice behavior. It appears noteworthy, that such magnetization features have not been observed in all studies of superconducting Ru-1212 [3,5,6]. In our case, we take into account the information, that Ru moments order antiferromagnetically in 2116 compounds [7–12] and the fact, that we used Sr-2116 as a precursor material for the preparation of Ru-1212. Thus, we decided to investigate the possibility, that the anomalies are due to Sr-2116 impurities, which could have been present in our Ru-1212 samples as a second phase in an amount $\leq 3\%$, in accordance with our X-ray results.

3.2 Magnetic study of $\text{Sr}_2\text{GdRuO}_6$

The samples of Sr-2116 were prepared as described above at the first step of the preparation of Ru-1212. Figure 4 shows the z.f.c. and f.c. magnetization taken in a field of 0.25 mT. The curves consist of a high temperature paramagnetic regime, where, as expected, the magnetization is a linear function of the magnetic field (*c.f.* figure 6b). At lower temperatures, a small anomaly of the magnetization is observed between 35 K and 30 K. The position of this cusp-like feature is marked by an arrow in figure 4 and in figure 5, where it is more clearly visible. From our low temperature structure data (figure 1b) we

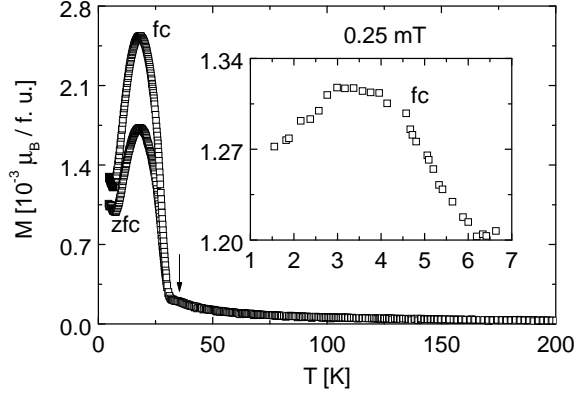


Fig. 4. Magnetic moment of Sr-2116 measured at 0.25 mT. Inset: the low temperature regime of the f.c. curve.

can exclude the possibility, that this slight cusp is related to a structural transition. Below 30 K, the magnetization begins to increase rapidly and reaches a peak at 18 K. A second peak of the magnetization is observed below 3 K, as shown in the inset of figure 4.

The temperature at which this second peak is observed is similar to the anti-ferromagnetic ordering temperature of the Gd moments in Ru-1212, as determined by neutron diffraction [18] and d.c. magnetization studies [4]. In order to exclude the possibility, that this second peak at 3 K or the cusp above 30 K are due to the trace impurities of cubic Gd_2O_3 present in the Sr-2116 sample, we also studied the magnetic properties of the Gd_2O_3 powder used for sample synthesis (Chempur 99.99 % pure). No transition was observed down to the lowest temperature investigated (1.6 K) in accordance with the report by Moon and Koehler [21].

Figure 5 shows, that the position of the cusp-like anomaly between 35 K and 30 K as well as that of the increase of the magnetization at 30 K are rather independent of magnetic field, while the position of the peak slightly shifts from 18 K at 0.25 mT down to 14 K at 35 mT and the magnetization decrease below the peak temperature becomes less pronounced. At 50 mT, the peak has disappeared and a ferromagnetic-like curve is observed. A f.c. magnetization curve taken at 200 mT (not shown) between 7 K and 300 K appears paramagnetic-like throughout the whole temperature range but the cusp in the 35-30 K temperature range is again clearly visible.

The hysteresis between the z.f.c. and f.c. curves (figure 4) is reminiscent of that observed for Ru-1212 and indicates, that Sr-2116 is not a simple anti-ferromagnet. As proposed for Ru-1212, such a behavior could be caused by a canted arrangement of the spins giving rise to a net magnetic moment. The presence of a ferromagnetic component is indicated by the hysteresis loop obtained at 16 K, which is shown in figure 6a. Using the remanent magnetization

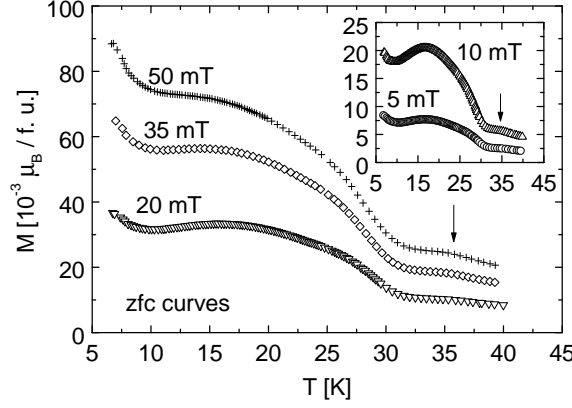


Fig. 5. The low temperature part of the z.f.c. d.c. magnetization curves of Sr-2116 in different magnetic fields.

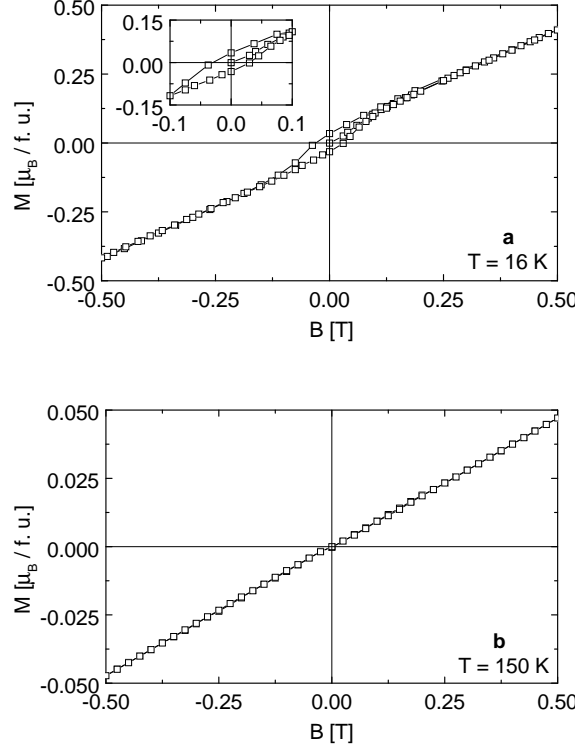


Fig. 6. d.c. magnetization measurements of Sr-2116 as a function of the magnetic field at (a) 16 K and (b) 150 K. Inset: the hysteresis loop in an extended scale.

as a measure of the spontaneous ferromagnetic moment this is $\sim 0.03 \mu_B$ per formula unit. We should note, that for the measurement in figure 6a the field was changed between 6 and -6 T. For clarity only the low field part of the measurement is presented.

A possible scenario for the explanation of these observations is the following: At about 35 K the expected [7–11] antiferromagnetic ordering of the Ru

moments takes place. Presumably, this corresponds to the 31 K ordering temperature of the Ru moments in Sr-2116 reported in literature [4,22]. A canting of the Ru moments creates an internal field, which at about 30 K polarizes the Gd moments leading to the observed rapid increase of the magnetization shown in figure 4. At about 18 K, Gd-Gd antiferromagnetic interactions start to dominate over this polarizing effect and the magnetization decreases. The ordering of the Gd moments takes place at about 3 K.

This interpretation of the data is consistent with a scenario proposed in [23] in order to explain the magnetic properties of Gd_2CuO_4 , where Cu orders antiferromagnetically at 260 K. Here, the canting of the Cu moments polarizes the Gd moments at about 100 K. Below 20 K, Gd-Gd interactions begin to dominate, while the actual antiferromagnetic ordering of the Gd moments, as indicated by specific heat and magnetization measurements, occurs at 6.5 K. In an applied magnetic field, the peak at 20 K is shifted to lower temperatures, similar to our results on Sr-2116 presented in figure 5, and finally merges with the one at 6.5 K, which is associated to the antiferromagnetic ordering of the Gd moments.

In a study of a series of Cu-doped 2116 compounds [24–28] superconductivity was observed, which appears to coexist with antiferromagnetic order of Ru^{5+} ions. A sharp increase of the susceptibility at 30 K similar to that in figure 4 was interpreted as the signature of ferromagnetic ordering due to double exchange between Ru ions of different valencies [24–26,28]. Double exchange was introduced by Zener [29] and in recent years represents a standard approach for the explanation of the transport and magnetic properties of the colossal magnetoresistance manganites, such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. There, the transfer of electrons through an oxygen ion between Mn ions of different valencies, namely 3+ and 4+, created through partial substitution of the trivalent La by divalent Sr, gives rise to a ferromagnetic coupling between these ions. In the 2116 compounds it was proposed, that partial doping with Cu, likely to be in the 3+ state, promotes the formation of Ru^{6+} ions. The double exchange mechanism would then involve Ru^{5+} and Ru^{6+} ions.

In the case of Sr-2116 studied here, it is difficult to visualize the origin of double exchange since no Cu doping is involved. On the other hand, Donohue and McCann [30], who prepared Sr-2116 compounds in a way similar to ours, report, that their sample was oxygen deficient with a composition of $\text{Sr}_2\text{GdRuO}_{5.95}$. Such a deficiency on the oxygen site could create Ru ions of different valencies and give rise to double exchange. Oxygen uptake during a heat treatment in oxygen atmosphere is then expected to affect the magnetic properties of such samples.

Following these ideas, we have treated the Sr-2116 sample used for the magnetization measurements presented in figures 4-6 for 5 days at 1060 °C in flowing

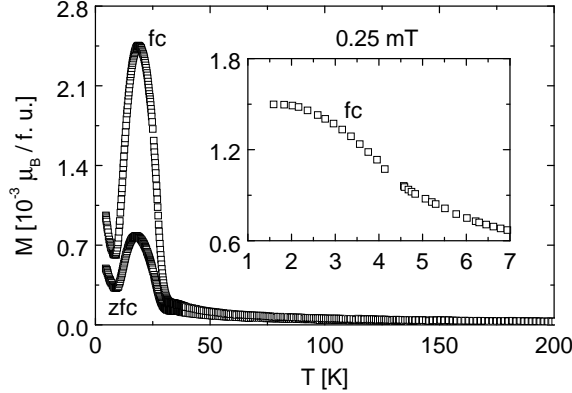


Fig. 7. z.f.c. and f.c. magnetization curves for the Sr-2116 sample of figure 4 after it was treated for 5 days in oxygen (see text). Inset: the low temperature part of the f.c. curve after the oxygen treatment.

oxygen. This treatment equals the second step in the preparation of Ru-1212 as described above (section 2). In figure 7 a pair of M-T curves is shown, which were taken after the oxygen treatment. It is obvious, that although all the features of the curves described so far are retained and the f.c. curve remains almost unchanged, the height of the z.f.c. peak is significantly reduced. Incorporation of oxygen to the sample would lead to a change of the valency of Ru ions towards the expected one of 5+. This would then suppress double exchange. A change of the valency of some Ru ions after the oxygen treatment would also change the Ru-Gd interactions in the sample. This could explain why the peak shown in the inset of figure 4, tentatively associated with Gd-moment ordering, appears now (figure 7) to be shifted to a lower temperature ≤ 1.6 K. The interaction of the Ru and Gd sublattices in Ru-1212 was recently discussed in [19].

On the basis of the above interpretation, the peak at 18 K must be related to the antiferromagnetic ordering of the Ru⁵⁺ moments. This is inconsistent with the reported [4,22] transition temperature. Within this scenario, the origin of the cusp in the magnetization curve between 30 and 35 K is unclear. It must also be mentioned, that the suppression of the z.f.c. magnetization seen in figure 7 could be related to a change in the morphology of the sample due to the long annealing times in flowing oxygen. In Ru-1212 [17] for example, the ratio of the domains with opposite sense of RuO₆-octahedra rotation is assumed to depend on the annealing of the sample.

3.3 Comparison between $RuSr_2GdCu_2O_8$ and Sr_2GdRuO_6

In view of the results presented so far it is very tempting to interpret the anomalies of the d.c. magnetization of Ru-1212 upon entering the supercon-

ducting state in terms of Sr-2116 impurities in the sample. The magnetization of Sr-2116 is similar to that of the anomalies of Ru-1212 and the temperatures of the magnetization peak observed for the two compounds differ only by about 3 K. A quantitative comparison can be done based on the mass susceptibilities or the magnetization per gram of the sample used for the measurements presented in figure 3, which may be supposed to be of unknown composition. The z.f.c. moment of Sr-2116 measured in a field of 0.25 mT (figure 4) is about $1.7 \times 10^{-3} \mu_B / (\text{f.u. Sr-2116}) \equiv 1.72 \times 10^{-5} \text{Am}^2/\text{g}$, while the peak increase above the z.f.c. “plateau” in the sample of figure 3a reaches $\sim 3.6 \times 10^{-3} \mu_B / (\text{f.u. Ru-1212}) \equiv 2.9 \times 10^{-5} \text{Am}^2/\text{g}$. In order to explain the z.f.c. anomaly observed in this sample in terms of Sr-2116 impurities one would thus need a mass of the impurity, which would correspond to 2.9/1.72 times the sample mass, which, of course, is impossible. Different estimates are reached, if a stronger moment of the Sr-2116 impurity is assumed, as detailed below.

On the basis of the assumption, that double exchange is causing the rapid increase of the magnetization for Sr-2116 at 30 K one might argue, that possible Sr-2116 impurities in the Ru-1212 sample have higher oxygen deficiencies than the sample of figure 4, which would give rise to more pronounced magnetization peaks without requiring large amounts of Sr-2116 impurities. One should keep in mind though, that possible impurities underwent an oxygen treatment during the last step of the preparation of Ru-1212. According to the result presented in figure 7 this would suppress double exchange.

Other impurities, that could be responsible for the observed magnetization peaks in the Ru-1212 sample are Ru-deficient Sr-2116 or Cu-doped Sr-2116. Such samples were also prepared and investigated with the result shown in figure 8. The sample of $\text{Sr}_2\text{GdRu}_{0.9}\text{O}_6$ was prepared in a way similar to the $\text{Sr}_2\text{GdRuO}_6$ sample. In order to simulate the most likely way of formation of Cu-doped $\text{Sr}_2\text{GdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ impurities in Ru-1212, a $\text{Sr}_2\text{GdRu}_{0.9}\text{O}_6$ sample was used as a precursor to which CuO was added. The pelletized mixture was heated at 1060 °C for 120 h in flowing oxygen. A comparison of the X-ray powder patterns of these samples (done on the Seifert diffractometer) with that of a Sr-2116 sample is shown in figure 1b. Although unidentified impurity peaks were present (together with Gd_2O_3 trace impurities for $\text{Sr}_2\text{GdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$), we decided to investigate these samples. The idea is, that, within the framework of double exchange for example, Ru deficiencies or Cu doping could enhance the magnetism of these compounds compared to that of Sr-2116. Indeed, as shown in figure 8 the magnetization of these compounds is enhanced with peaks at about 20 K, while no low temperature peak was observed in the f.c. curves, which could be associated to Gd ordering in these compounds. A quantitative analysis of the results, similar to the one above for Sr-2116, using a moment of $4 - 6 \times 10^{-3} \mu_B / \text{f.u.}$ (figure 8) leads to similar result, that a large fraction of the sample (50-70%) would have to consist of the impurity phase. Given the single-phase nature of the x-ray powder pattern, which was taken

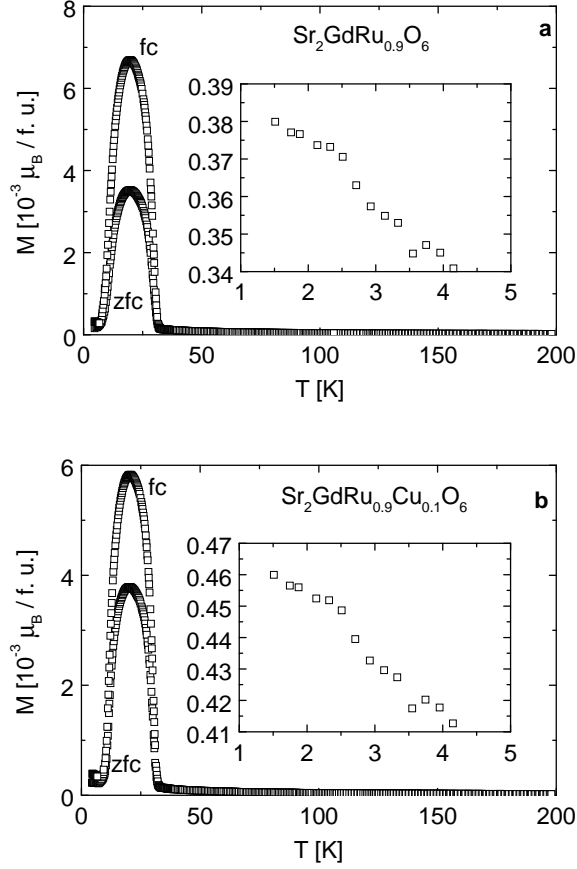


Fig. 8. d.c. magnetization curves in a measuring field of 0.25 mT of (a) $\text{Sr}_2\text{GdRu}_{0.9}\text{O}_6$ and (b) $\text{Sr}_2\text{GdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ (nominal compositions).

on the sample used for the magnetic measurements presented in figure 3, this is impossible.

For the $\text{Sr}_2\text{GdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sample no indication of superconductivity was observed in our d.c. magnetization measurements unlike the report for other Cu doped 2116 compounds [24–28]. It must be mentioned, however, that these superconducting samples were prepared at a much higher temperature of about 1400 °C and that a similar sample with Ba in the place of Sr, although it was prepared at high temperatures, did not show superconductivity [27].

4 Concluding remarks

In summary, we have observed distinct anomalies in the d.c. magnetization curves of Ru-1212 upon entering the superconducting state. In order to determine whether these anomalies could be due to Sr-2116 impurities in the sample, an extensive study of the magnetic properties of Sr-2116 in terms of

d.c. magnetization measurements was carried out. The magnetic properties of Sr-2116 are described according to the following scenario: At ~ 35 K the Ru moments order antiferromagnetically but in a canted arrangement. This canting of the Ru moments creates an internal field, which polarizes the Gd moments, leading to a rapid increase of the magnetization at about 30 K. At ~ 18 K, Gd-Gd antiferromagnetic interactions start to dominate the polarizing effect and the magnetization decreases. The actual antiferromagnetic ordering of Gd takes place at about 3 K. An alternative (less likely) scenario for the explanation of the data based on double exchange between Ru ions of different valencies was also presented.

In addition to (nominally) stoichiometric Sr-2116, the magnetization of Ru-deficient and Cu-doped Sr-2116 compounds was also measured; no indication for superconductivity of the Cu doped Sr-2116 compound was found in d.c. magnetization measurements.

Although similarities were observed in the magnetic behavior of Sr-2116 and the magnetization peaks of the Ru-1212 sample, a direct quantitative comparison clearly revealed, that very large amounts of Sr-2116 (or the related compounds studied), easily detected by X-ray powder diffraction, would be required for the explanation of the magnetization peaks in terms of impurities present in the sample. Since no such amounts were observed, the peaks are rather an intrinsic property of Ru-1212. The proposals of Klamut *et al.* [20] for the explanation of this property were mentioned above in section 3.1. The fact, that from our data and the data presented in [20], the onset of the peaks occurs at the temperature where inter-granular coupling is established indicates, that the effect is related to superconductivity. An alternative explanation based on the scenario presented above for the magnetic behavior of Sr-2116 is the following: In Ru-1212, the Ru moments order antiferromagnetically at ~ 135 K in a canted arrangement, which creates an internal field, that in turn polarizes the Gd moments at low temperatures (~ 25 K). Below 25 K, a combination of the polarizing effect, the Gd-Gd antiferromagnetic interactions and the effect of superconductivity leads to the observation of the peak-like feature. In any case, an open question is why this low temperature peak in the magnetization curve of Ru-1212 is not observed [3,5,6] in all d.c. magnetization studies of Ru-1212. A more detailed investigation of the magnetic properties of Ru-1212 samples similar to that presented in section 3.1 of this paper, which could provide an answer to this question and clarify the origin of the observed peaks, is now in progress and details will be published in the near future.

5 Acknowledgments

We thank Wolfgang Ettig and Armin Dertinger for their valuable technical support and help.

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